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The influence of "small molecules" on crystallization of TiO_2 xerogels

Jana Pagáčová[a,*], Alfonz Plško[b], Katarína Michalková[b], Vladimíra Zemanová[b], Iveta Papučová[a]

[a]*Alexander Dubček University of Trenčín, Faculty of Industrial Technologies in Púchov, I. Krasku 491/30, 020 01 Púchov, Slovakia*
[b]*Alexander Dubček University of Trenčín, Študentská 2, 91150 Trenčín, Slovakia*

Abstract

The sol-gel method was used for preparation of sols and the precursor sols were prepared from a mixture of titanium(IV) tetra-isopropoxide, isopropanol, water, nitric acid and "small molecule" as stabilizing reagent. The acetylacetone and acetic acid were used as small molecules ("stabilizers"). Three TiO_2 xerogels were studied by DTA–TG analysis in combination with the XRD analysis. The crystallization was determined by non-isothermal analysis. The values of activation energy of crystallization were calculated using Johnson-Mehl-Avrami model. For xerogel without "small molecules" and xerogel with acetic acid, the activation energy of anatase crystallization is $E = (1.07 \pm 0.02) \cdot 10^5$ J.mol^{-1} and $E = (0.78 \pm 0.02) \cdot 10^5$ J.mol^{-1}, respectively. According to Avrami coefficient $M \sim 1$ for both xerogels, the mechanism of crystallization is surface nucleation. There is no crystallization of anatase in xerogel with acetylacetone.

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Keywords: TiO_2; xerogel; DTA–TG; XRD; crystallization

1. Introduction

The titanium dioxide exhibits very interesting properties (chemical stability, mechanical hardness, high refractive index, low absorption coefficient, high transparency in VIS and near IR, wide band gap, etc.) which make it attractive for preparation in form of coatings. The coatings are useful for applications in various fields relating to

* Corresponding author. Tel.: +421 42 2851 864.
E-mail address: jana.pagacova@fpt.tnuni.sk

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protective, reflection, antireflection, antibacterial and self-cleaning films, optics, sensors, etc. [1–5]. During thermal treatment of coatings prepared by sol-gel method, the decomposition of precursors leads to formation of TiO_2 and its subsequent crystallization. These processes are influenced by the presence of various reagents which stabilise the initial sols [6, 7]. The better understanding of the thermal behaviour of gels formed in sol-gel process is important because it influences the transition of sol to gel and xerogel in coatings and thus influences the final surface properties of coatings.

TiO_2 has three crystal forms – anatase, rutile and brookite. The formation of particular forms depends on many factors, such as nature of starting precursors, composition of sol, deposition method and annealing temperature. The sol-gel process predominantly produces amorphous TiO_2 which is transformed to anatas during thermal treatment over the temperature of 450 °C [8, 9] and some authors [10–12] report anatase crystallization from the temperature of 350 °C. The anatase to rutile transformation usually takes place at temperatures of 600–800 °C [11, 13] even after addition of acetylacetone [14].

The kinetics of crystallization is mostly interpreted in terms of the nucleation growth model formulated by Avrami [15–17]. This model describes the time dependence of the fractional crystallization in the following form:

$$\alpha = 1 - \exp[-(kt)^m] \tag{1}$$

where α is the conversion of the crystallization with respect to time, t, and k and m are constants. The constant m may be interpreted in terms of the number of crystal growth dimensions. After the differentiation with respect to time, the Johnson-Mehl-Avrami-Kolmogorov (JMAK) rate equation is obtained [18, 19]:

$$\frac{d\alpha}{dt} = km(1-\alpha)[-\ln(1-\alpha)]^{\left(1-\frac{1}{m}\right)} \tag{2}$$

The validity of Eq. (2) is based on the assumptions that the crystallization is carried out under isothermal conditions and that homogeneous nucleation or heterogeneous nucleation at randomly dispersed pre-existing nuclei can be observed. Further, it is assumed that the growth rate of crystals is independent of time and is the same in all directions (isotropic crystal growth). The temperature dependence of k is the other component of the kinetic equation for the heterogeneous reaction in the solid state. The Arrhenius equation, Eq. (3), has been widely applied to a range of chemical kinetic phenomena taking place in the solid state, including crystallization:

$$k(T) = A\exp\left[-\frac{E}{RT}\right] \tag{3}$$

where A is the pre-exponential factor, E is the activation energy, T is the thermodynamic temperature and R stands for the gas constant. The model-fitting approach assumes that the mechanism of the process is known and the rate equation is derived with the respect to the knowledge of the process mechanism [20, 21].

In this paper, the influence of acetylacetone and acetic acid ("small molecules") on crystallization of TiO_2 xerogels was studied by DTA and XRD analyses.

2. Experiment

For synthesis of TiO_2 sols, titanium(IV) isopropoxide (98 %, $Ti(iPr)_4$), isopropanol (p.a., IPA), nitric acid (66 %, HNO_3) and distilled water (H_2O) were used. The acetylacetone (p.a., AcAc) and acetic acid (99 %, AA) were used as stabilizing reagents called "small molecules". The molar composition of the solutions used for preparation of sols is shown in Table 1. The sols were prepared from three solutions. The first solution (A) was prepared from $Ti(iPr)_4$ and 40 % of IPA. The second solution (B) was prepared from HNO_3, H_2O and 40 % of IPA. The third solution (C) consisted of 20 % of IPA for TiO_2(1) sol or mixture of "small molecules" and IPA for TiO_2(1)+AA and TiO_2(7) sols. The solution (A) was added drop by drop into the solution (B) and obtained mixture was stirred for 15 min. Then the given solution (C) was also added drop by drop into the solution and obtained mixture was stirred for 15 min [22, 23].

After the fourteen days from sol preparation, the xerogels were prepared by drying of sols at temperature 80 °C until their constant weight was obtained. Then the xerogels were crushed, sieved and stored in environment with relative humidity of 52.9 %.

Table 1. Molar composition of solutions used for preparation of sols.

Sol	Component					
	TiO_2	AcAc	AA	HNO_3	H_2O	IPA
TiO_2(1)	0.05	0	0	0.090	0.210	0.65
TiO_2(7)	0.05	0.12	0	0.054	0.126	0.65
TiO_2(1)+AA	0.05	0	0.03	0.080	0.190	0.65

Thermal behaviour of TiO_2 xerogels was studied using NETZSCH STA 449 F1 Jupiter instrument in temperature range 30–1000 °C at heating rate 10 °C.min^{-1}. Xerogels (~200 mg, fraction 200–315 μm) were placed in alumina crucibles. The measurements were carried out in N_2 atmosphere (20 ml.min^{-1}). The Al_2O_3 was used as a reference material. The crystallization experiments were performed at the heating rates (2.5, 5.0, 7.5, 10.0, 12.5) °C.min^{-1}.

DTA curves were processed according to [24]. After obtaining $\alpha(T)$ and $d\alpha(T)/dT$ from DTA curve for constant rate heating regime, the empirical form of JMAK rate equation with the Arrhenius dependence on temperature, Eq. (4), was considered as basic crystallization kinetic equation:

$$\beta \frac{d\alpha}{dT} = A \exp\left[-\frac{E}{RT}\right] M(1-\alpha)\left[-\ln(1-\alpha)\right]^{\left(1-\frac{1}{M}\right)} \tag{4}$$

where β is the constant heating rate, α is the conversion of the crystallization, A is the pre-exponential factor, E is the activation energy of the crystallization, T is the thermodynamic temperature, R is the molar gas constant and M is Avrami coefficient which may be interpreted in terms of the number of crystal growth dimensions or crystal growth mechanism [25].

The values of kinetic parameters (A and E) and Avrami coefficient M were calculated by two-step process of regression analysis. As the first, the Eq. (4) was linearized and the linear least squares problem was solved. The next step was connected with solving of non-linear least squares problem using Eq. (4). The results of linear regression were used as the starting values of optimized parameters. MATLAB® software was used for calculations.

XRD patterns of samples were recorded with PANanalytical Empyrean X-ray diffractometer using CuKα radiation. XRD analysis was carried out for powder xerogels after isothermal treatments at (400, 450, 500, 550) °C for 60 min as well as samples annealed at 1100 °C (after non-isothermal analysis). The heating rate for mentioned temperatures was 10 °C.min^{-1}. The data were collected for the 2θ range of 15–35° and 20–75°, respectively.

3. Results and discussion

The DTA–TG curves of samples without and with “small molecules” are presented in Fig. 1. DTA curves of xerogel without stabilizing reagent and xerogel with acetic acid are similar (Fig. 1a and 1b). Up to temperature about 200 °C, there is a broad endothermic peak with minimum about 140 °C. This peak represents the loss of water and solvent [6, 8, 13]. The peak about 250 °C is attributed to the decomposition of present organic compounds as well as the subsequent reactions of decomposed products [8, 13, 26]. The exothermic peaks with maxima about 390 °C were attributed to the anatase crystallization [13, 26, 27]. Last peaks at 760 and 800 °C correspond to the crystallization of rutile phase [10, 13, 28]. The DTA curve of xerogel with acetylacetone is different. The maximum of endothermic peak is at lower temperature, near 110 °C, and there are only two exothermic peaks with maxima about 210 and 465 °C. The first sharp peak is probably caused by decomposition of the large portion of organics. According the temperature, the second exothermic peak could be attributed to the crystallization of anatase but because there is not peak of rutile, it is probably caused by the further decomposition of the organics, possibly some more stable acetylacetonate compounds or products of previous decomposition.

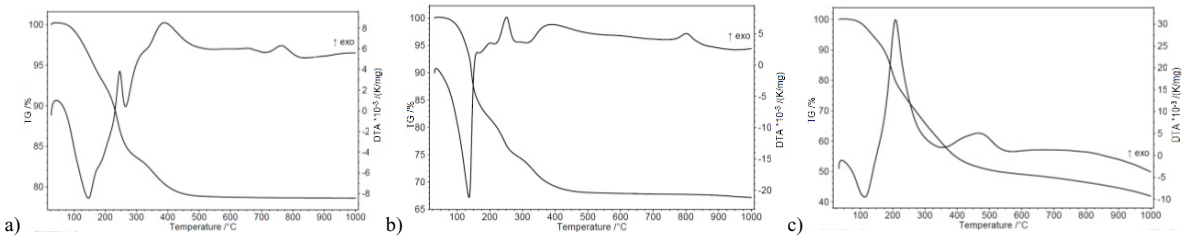

Fig. 1. DTA/TG curves of xerogel: a) TiO_2(1), b) TiO_2(1)+AA, c) TiO_2(7).

The main features of the TG curves are quite similar for the xerogel without stabilizer and xerogel with acetic acid, while they are different from the sample with acetylacetone. According to the measurements, the total mass loss of xerogels without stabilizer, with acetic acid and with acetylacetone was about 21, 33 and 58 wt. % (Table 2). According to TG, the mass loss could be occurred in four temperature ranges which are practically similar for first two xerogels. Except of the first range for the second xerogel in which the mass loss is higher probably on the basis of release of free acetic acid. Decomposition of these two xerogels is practically completed by 500 °C. On the other hand, the temperature ranges of mass loss for xerogel with acetylacetone are quite different. While mass loss in the first range is similar to xerogel without stabilizer, other mass losses are significantly higher. The mass loss 7.5 % in the range from 570 to 1000 °C indicates that the decomposition processes are still in the progress. For xerogel with acetylacetone, the main mass loss is shifted to the temperature range near 600 °C, while the mass loss is the most significant "only up to" near 300 °C for xerogels without stabilizer and with acetic acid.

Table. 2. Decomposition steps and mass of TiO_2 xerogels.

Sample	Temperature range (°C)	Mass loss (%)	Total mass loss (%)
TiO_2(1)	30–190	6.88	21.40
	190–300	9.49	
	300–500	4.77	
	500–1000	0.26	
TiO_2(1)+AA	30–200	18.35	32.83
	200–285	6.93	
	285–490	6.6	
	490–1000	0.94	
TiO_2(7)	30–150	6.68	58.11
	150–245	19.68	
	245–570	24.22	
	570–1000	7.53	

For confirmation of above mentioned assumptions about course of crystallization in studied samples, the XRD analysis of different thermally treated xerogels was performed. The X-ray diffraction analysis of samples after isothermal treatment of xerogels at (400, 450, 500 and 550) °C confirmed the presence the main diffraction peaks of anatase around $2\theta = 25.3°$ [11, 14, 27, 28] in samples without stabilizer and with acetic acid (Fig. 2ab). In contrast, there is no diffraction peak of anatase in the samples with acetylacetone at all temperatures of isothermal treatment, as it can be seen in Fig. 2c. Moreover, the XRD analysis of sample annealed at 1100 °C (after non-isothermal analysis) also showed no rutile phase in sample with acetylacetone (Fig. 3), while there is the rutile in samples without stabilizer and with acetic acid [13, 14].

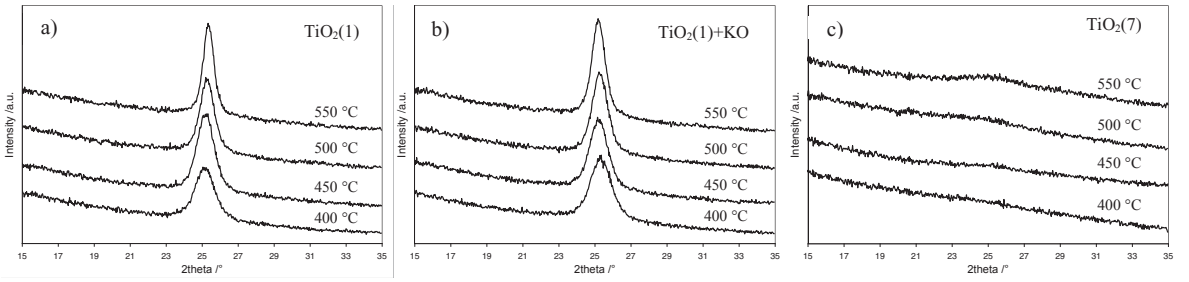

Fig. 2. XRD patterns of xerogels after isothermal treatments: a) $TiO_2(1)$, b) $TiO_2(1)$+KO, c) $TiO_2(7)$.

On the basis of facts mentioned above, the crystallization occurs in xerogels without stabilizer and with acetic acid and DTA peak in temperature range of (390–400) °C and (760–800) °C is associated with crystallization of anatase and rutile, respectively. In xerogel with acetylacetone, the peak near temperature of 465 °C cannot be considered as the peak of anatase crystallization. It is much better to associate it with the formation and subsequent decomposition of various carbidic compounds. It is also indirectly confirmed by the mass loss which is localized in area to 600 °C for sample with acetylacetone.

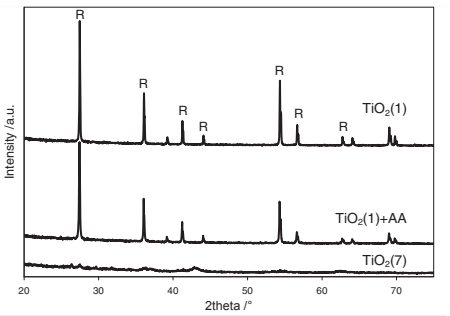

Fig. 3. XRD patterns of xerogels annealed at 1100 °C.

The kinetics of crystallization was studied for two xerogels in which the anatase formation was confirmed. Fig. 4 shows DTA curves of xerogels without “small molecule” and with acetic acid measured at various heating rates. The kinetic parameters and Avrami coefficient calculated using Eq. (4) are summarized in Table 3. The activation energy of anatase crystallization for xerogel with acetic acid is lower than activation energy for xerogels without stabilizer. However, the acetic acid does not influence the mechanism of crystallization (surface nucleation mechanism) because constant *M* has the value near 1 in both cases [25].

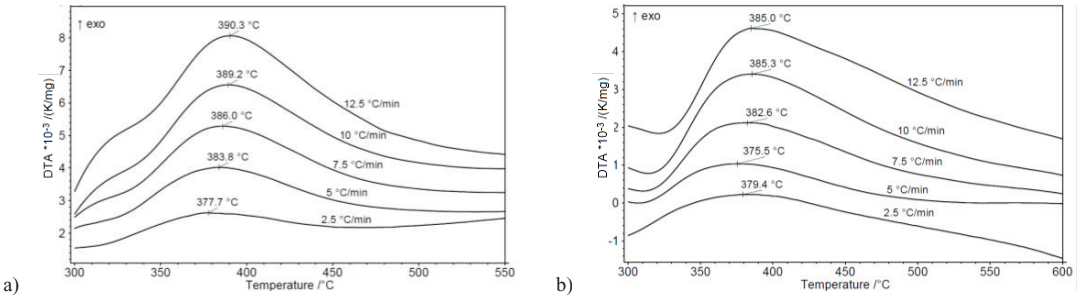

Fig. 4. DTA curves of a) $TiO_2(1)$ xerogel and b) $TiO_2(1)$+AA xerogel at various heating rates.

Table. 3. The kinetic parameters of crystallization and Avrami coefficient of samples.

Xerogel	$A \cdot 10^{-6}$ (min^{-1})	$E \cdot 10^{-5}$ (J.mol^{-1})	M	Sum of squares
TiO_2(1)	53.7 ± 22.0	1.07 ± 0.02	1.008 ± 0.013	0.4842
TiO_2(1)+AA	0.19 ± 0.05	0.78 ± 0.02	1.015 ± 0.012	0.2057

4. Conclusion

Based on DTA–TG curves and XRD analysis it was found that the whole course of decomposition processes as well as crystallization is practically the same for xerogel with acetic acid in comparison with xerogel without stabilizing reagent (without "small molecules"). However, the acetylycetone in system influences the course of processes during thermal treatment in such way, that the anatas crystallization does not occur and whole decomposition process is probably associated with the formation of carbidic compounds.

In TiO_2 xerogel without "small molecules", the crystallization of anatase occurs in temperature interval 350–450 °C. From Johnson-Mehl-Avrami model, the activation energy of anatase crystallization is $E = (1.07 \pm 0.02) \cdot 10^5$ J.mol^{-1}. According to Avrami coefficient M (~ 1), the mechanism of crystallization is surface nucleation.

The acetic acid does not influence the main DTA and TG features and increases the total mass loss especially at the beginning of heating. The acetic acid influences the crystallization process of anatase by decreasing of energy barrier of crystallization ($E = (0.78 \pm 0.02) \cdot 10^5$ J.mol^{-1}). However, the acetic acid does not influence the mechanism of crystallization.

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